Experimental and Computational Studies of Molecular and Lattice Symmetries of Energetic Materials at High Pressure

Suhithi (Su) Peiris

Research and Technology Department

Naval Surface Warfare Center - Indian Head Division

Indian Head, Maryland 20640

Report Documentation Page		*Form Approved* *OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **2002**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**	
4. TITLE AND SUBTITLE **Experimental and Computational Studies of Molecular and Lattice Symmetries of Energetic Materials at High Pressure**		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Surface Warfare Center - Indian Head Division, Research and Technology Department Indian Head, MD 20640**		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release, distribution unlimited**			
13. SUPPLEMENTARY NOTES **The original document contains color images.**			
14. ABSTRACT			
15. SUBJECT TERMS			

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT **SAR**	18. NUMBER OF PAGES **18**	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**			

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Overall Research Objectives

To study energetic materials of interest to the Navy/DoD at the high-pressure and high-temperature of detonation.

- **To study the initiation mechanism of detonation**

- **To learn the phase, lattice, and molecular symmetry, and measure theoretical maximum density (TMD) of a material at high pressure and temperature just before initiation**

- **To understand exactly what chemical bonds are most energetic and why, at the pressure and temperature of detonation**

- **To model the global kinetics and reaction mechanisms of energetic materials during detonative reactions**

Impact of this Basic Research

• This research generates phase and density data essential for **deciding if a new material could be used in a weapon**

• The relevant data and thermodynamic parameters for each material is presented and published **to enhance predictive modeling** and simulation software.

• The results **transition into all areas of energetic materials systems** in keeping with the NAVSEA Grand Challenges of:
  • Sixth Generation Energetics
  • Assured Lethality/effects
  • Scalable Combat Power Materials

• Successful completion of the goals of this program will help develop Navy After Next enabling technologies such as:
  • High Strength Materials
  • Long-life, High-Energy, Insensitive, Solid Propellants
  • Energetic Structural Composites
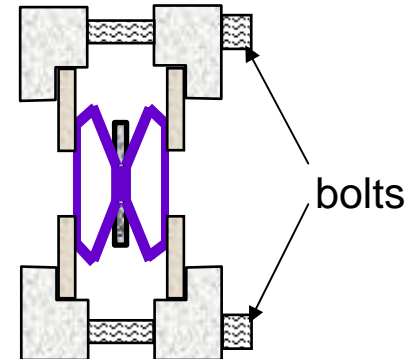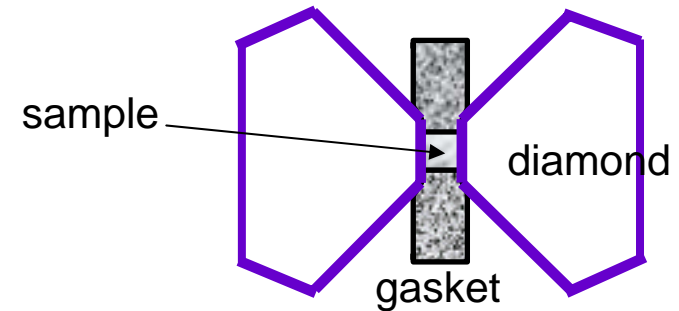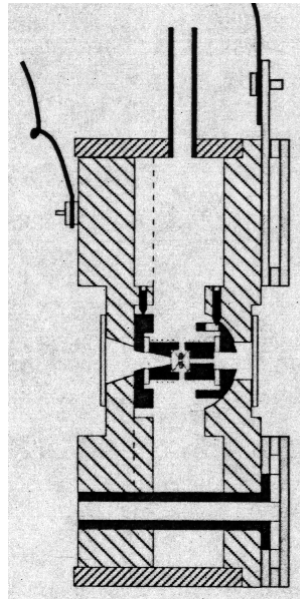
NAVSEA
INDIAN HEAD
Surface Warfare Center Division

Experimental Methodology

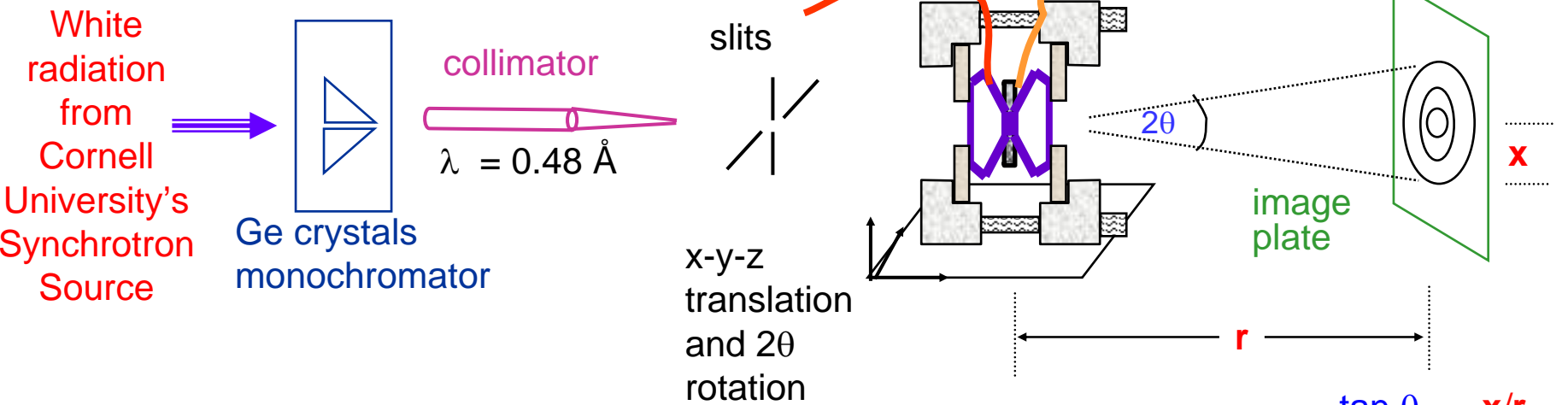Use **Diamond Anvil Cells** (DAC) with coil Heaters (HDAC) to achieve

• High pressures (P) to 10 GPa (100 kbars)

• High temperatures (T) to 300°C (up to 1000 °C possible under Argon)

• Any P, T in that range

HDAC

sample — diamond

gasket

bolts

NAVSEA
INDIAN HEAD
Surface Warfare Center Division
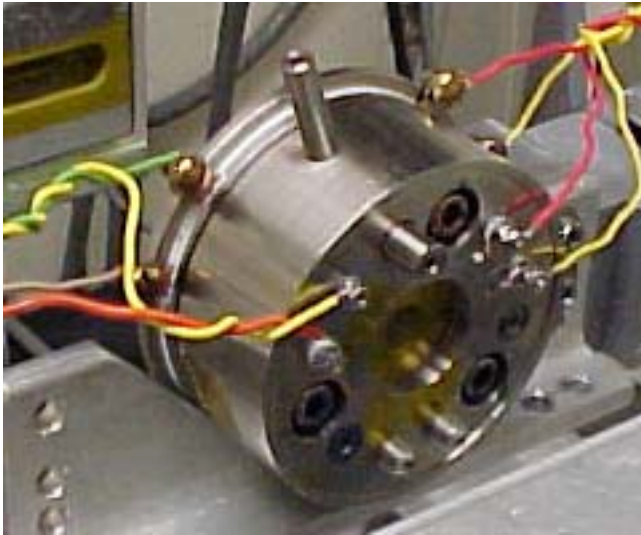
Angle-Dispersive X-ray Diffraction

White radiation from Cornell University's Synchrotron Source

Ge crystals monochromator

collimator

$\lambda = 0.48$ Å

slits

x-y-z translation and 2θ rotation

2θ

image plate

$\textbf{x}$

$\textbf{r}$

$\tan\theta = \textbf{x/r}$

$d = \dfrac{\lambda}{2\sin\theta}$.

Micro-Raman Spectroscopy

CCD

3/4 m double spectrometer

Ar$^+$ Laser

Microscope optics

Pressure Cell

Microscope stage

Research and Technology Department

Dynamics and Diagnostics Division, Static High-Pressure Group
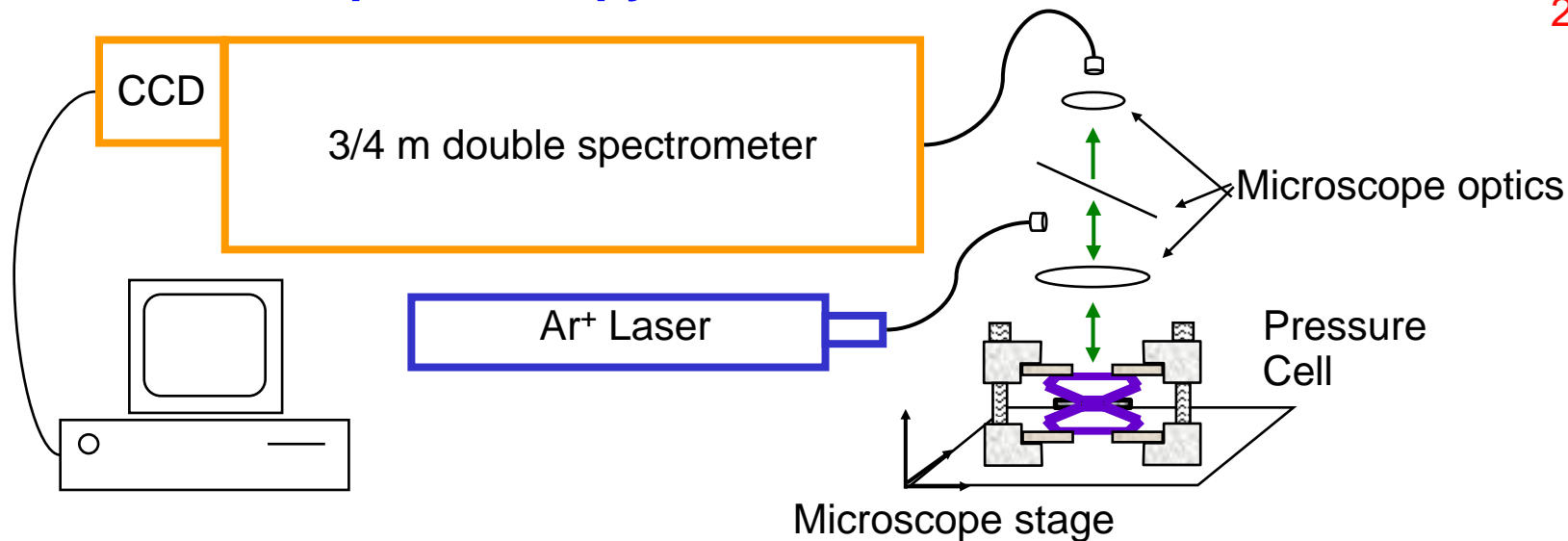
Theoretical Method

- The zero degree isotherm may be calculated directly from ab-initio techniques

- Both Hartree-Fock method and Density Functional Theory have been used

- Commercially available computer programs such as GAUSSIAN 98[i] and CRYSTAL 98[ii] provide a starting point

- Rigid molecule approximation with additional refinements such as:

  – Self-consistent geometry optimization (the crystalline lattice and the molecule structure)

  – Electronic correlation corrections to correct the total energy

- Calculations require state of the art computational capability and sometimes take 2-4 days to complete
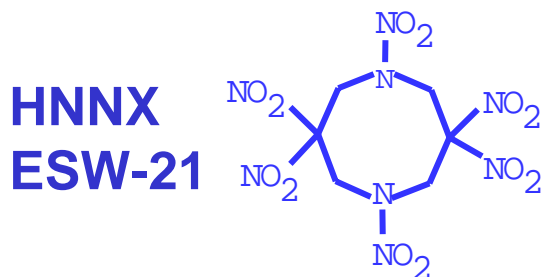
[i]. A. Frisch, M. J. Frisch, *GAUSSIAN98 User's Reference* (Gaussian, Inc., Pittsburgh, 1998).

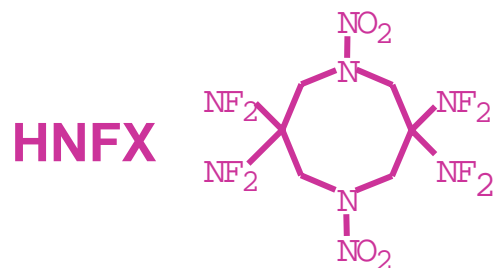[ii]. R. Dovesi, V. R. Saunders, C. Roetti, et al., *CRYSTAL98 User's Manual*, University of Torino.

NAVSEA
INDIAN HEAD
Surface Warfare Center Division

Results - Comparison of HMX, -NO$_2$ and -NF$_2$ analogs

HMX
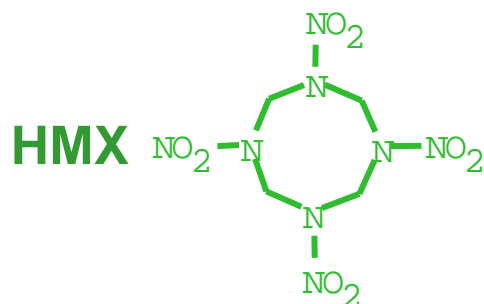
β-HMX = Monoclinic structure
2 molecules/unit cell
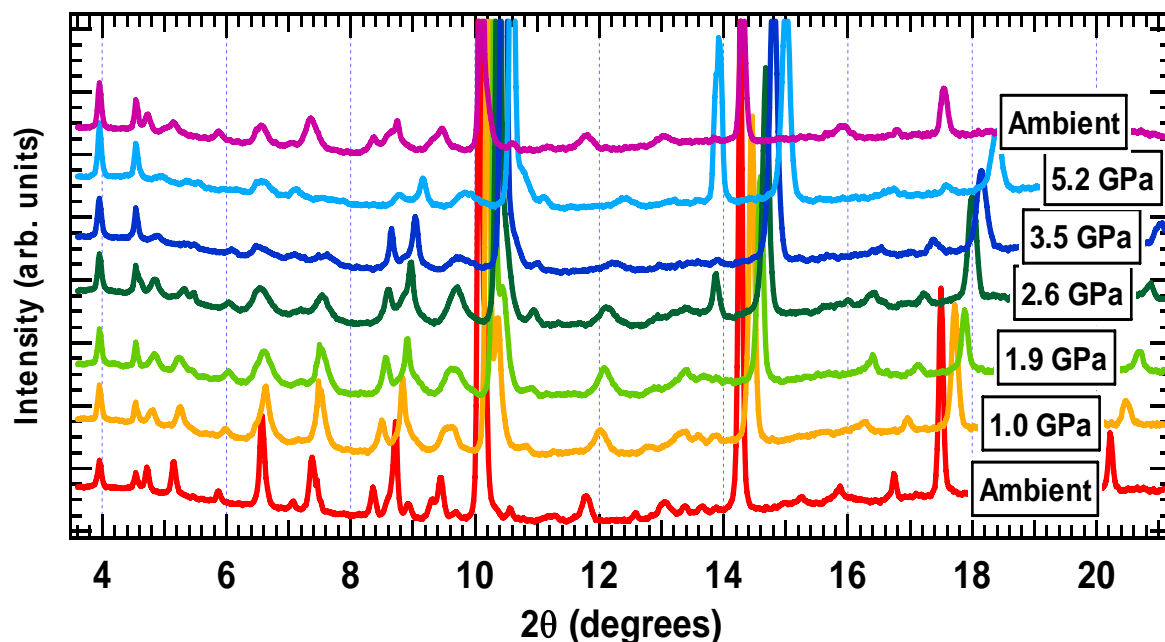ambient P,T density=1.91 g/cc

HNNX
ESW-21

HNNX or ESW-21 = Orthorhombic structure
4 molecules/unit cell
ambient P,T density=1.86 g/cc

HNFX

HNFX = Rhombohedral structure
9 molecules/unit cell
ambient P,T density=1.81 g/cc

HMX Compression at Ambient Temperature

Intensity (arb. units) vs 2θ (degrees) plot with curves labeled:
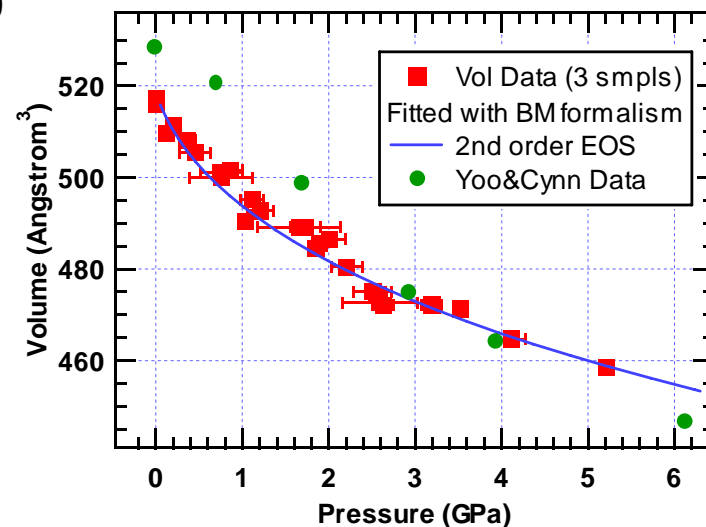- Ambient (magenta)
- 5.2 GPa (cyan)
- 3.5 GPa (blue)
- 2.6 GPa (dark green)
- 1.9 GPa (green)
- 1.0 GPa (orange)
- Ambient (red)

β-HMX is monoclinic with space group: $P2_1/c$

3rd order Birch-Murnaghan Equation of State yields :
Bulk Modulus: 8.9 GPa
Derivative: 46.5

Previous study by Yoo and Cynn (LLNL)
Bulk Modulus: 14.4 GPa Derivative: 13.3
non-hydrostatic using 7 data points to 10GPa

• We have a lot more (26) lower-pressure data.
• Also our data is on RDX-free HMX.
• Our V_0 = 518 Å^3 as published in ICDD.

Volume (Angstrom^3) vs Pressure (GPa) plot legend:
- Vol Data (3 smpls) Fitted with BM formalism
- 2nd order EOS
- Yoo&Cynn Data

NAVSEA
INDIAN HEAD
Surface Warfare Center Division

HNNX Compression at Ambient Temperature
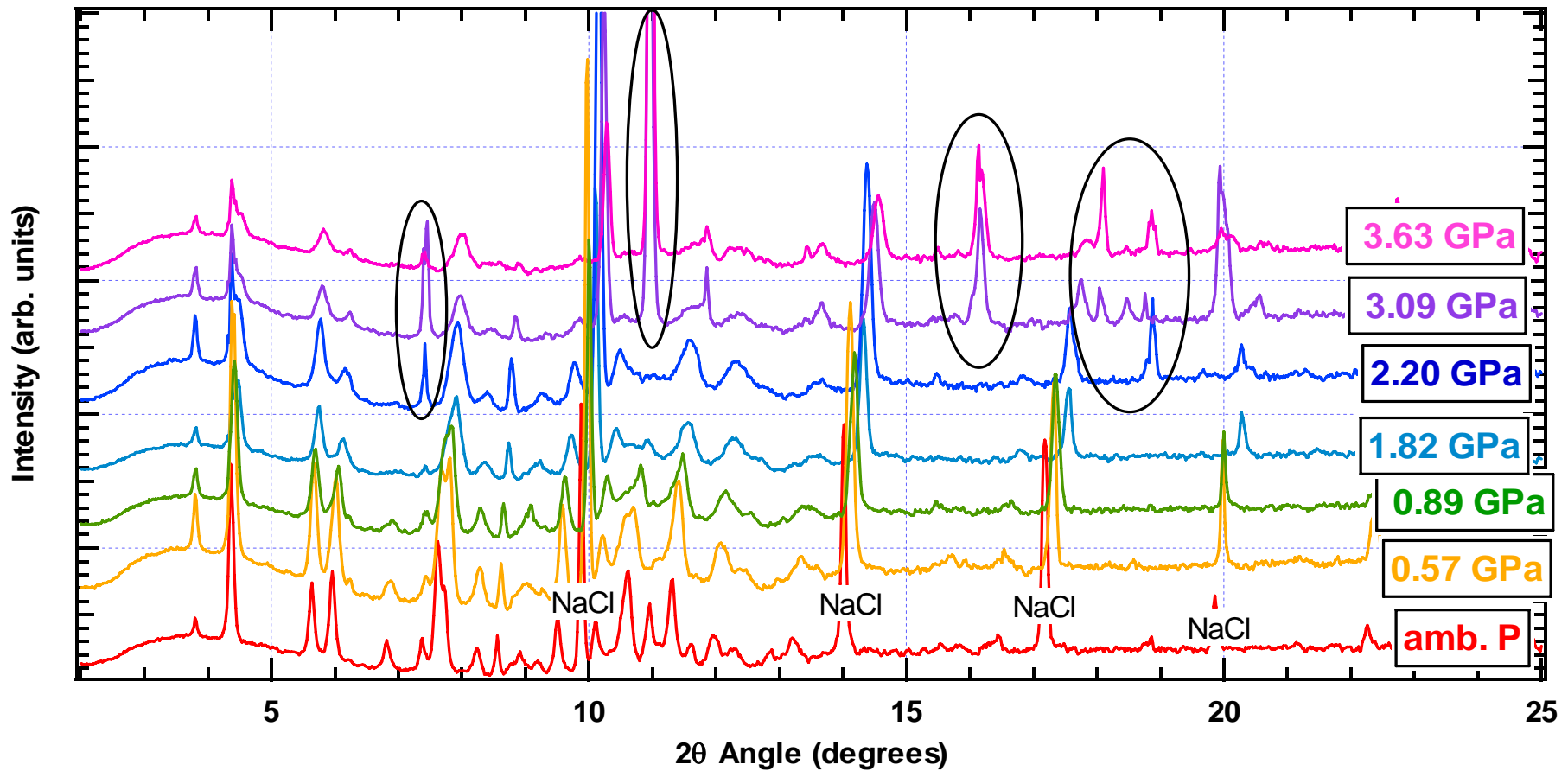
- Ambient pressure orthorhombic lattice is stable to about 2.2 GPa.
- Above that pressure new peaks appear indicating a phase transition.

Research and Technology Department

Dynamics and Diagnostics Division, Static High-Pressure Group

Isothermal EOS of HNNX
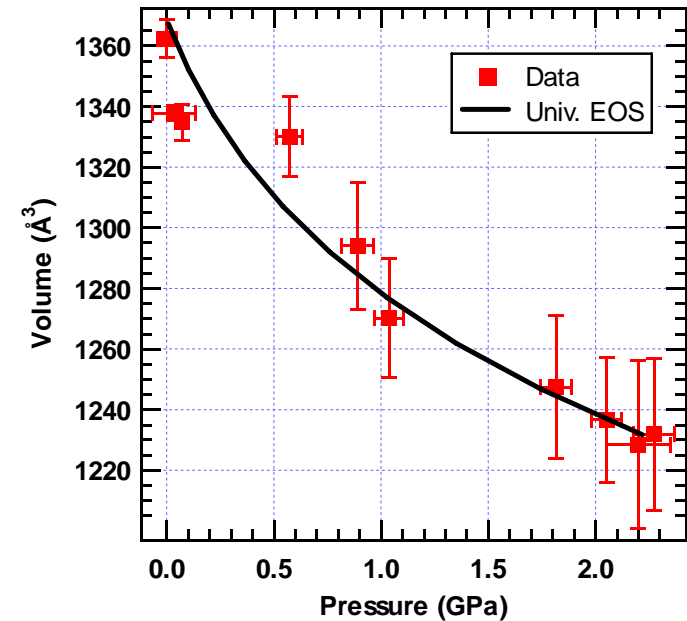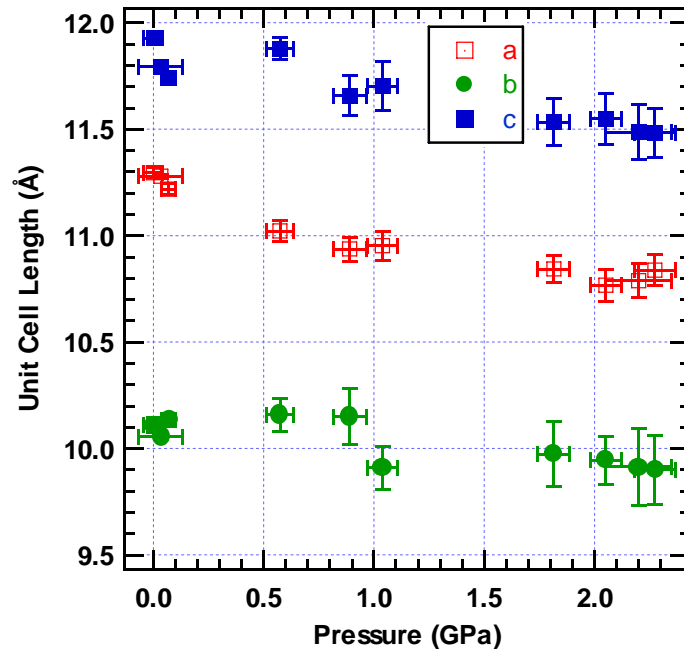
• The compression of the unit cell a, b and c axes flatten towards 2.0 GPa also indicating a phase transition

• Above 2.3 GPa, the ambient pressure orthorhombic lattice can no longer be assumed.

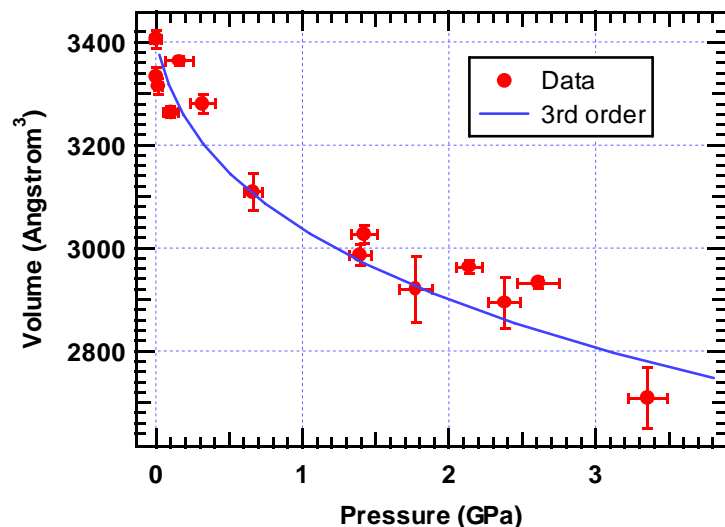Univ. EOS formalism (using data to 2.3 GPa):

$K_0 = 7.46 \pm 2.45$ GPa

$K_0' = 20.0 \pm 7.3$

Research and Technology Department

Dynamics and Diagnostics Division, Static High-Pressure Group

HNFX Compression at Ambient Temperature
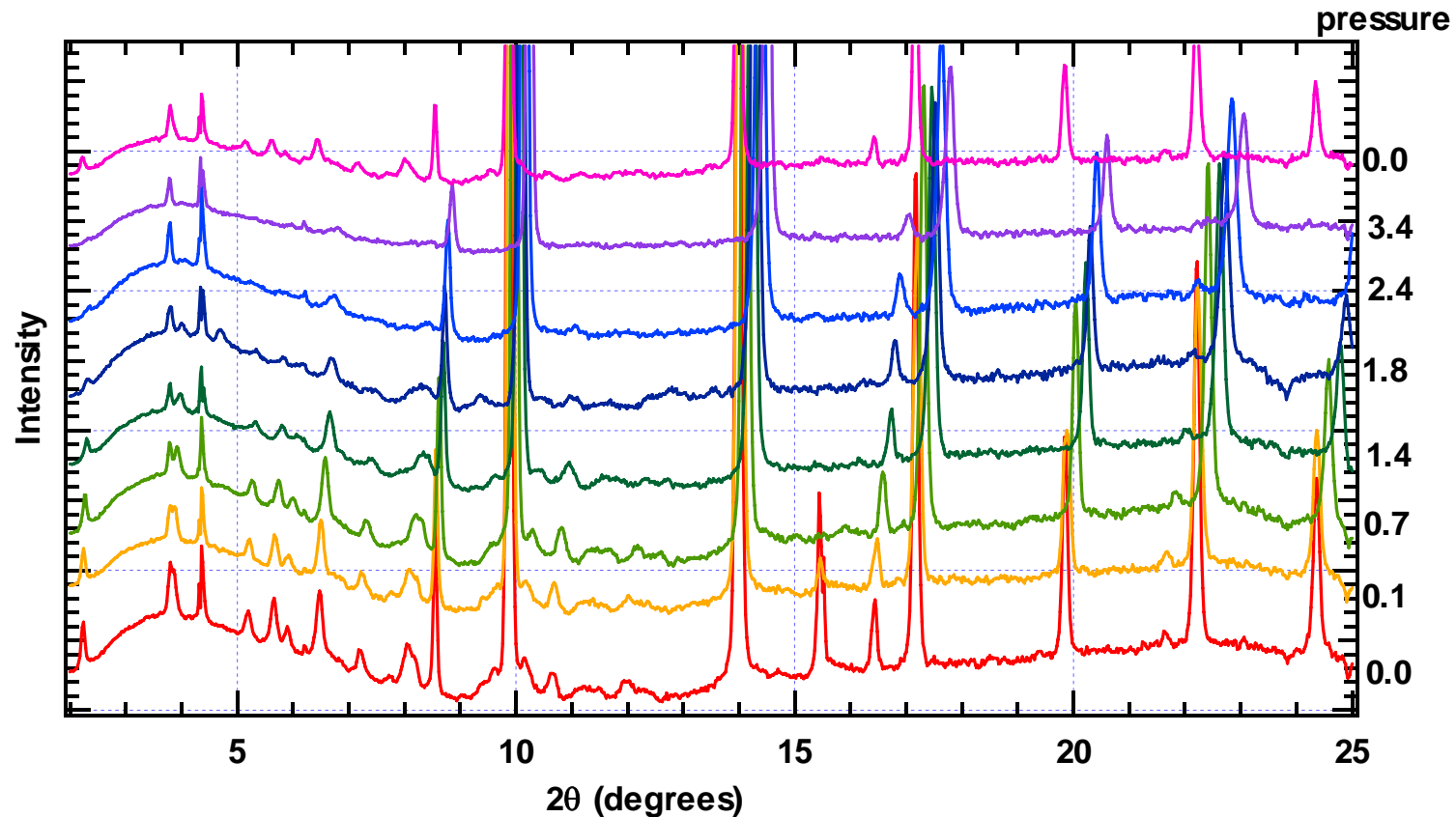
- The ambient pressure Rhombohedral (R-3) lattice is stable to 3.4 GPa, the highest pressure achieved in study.
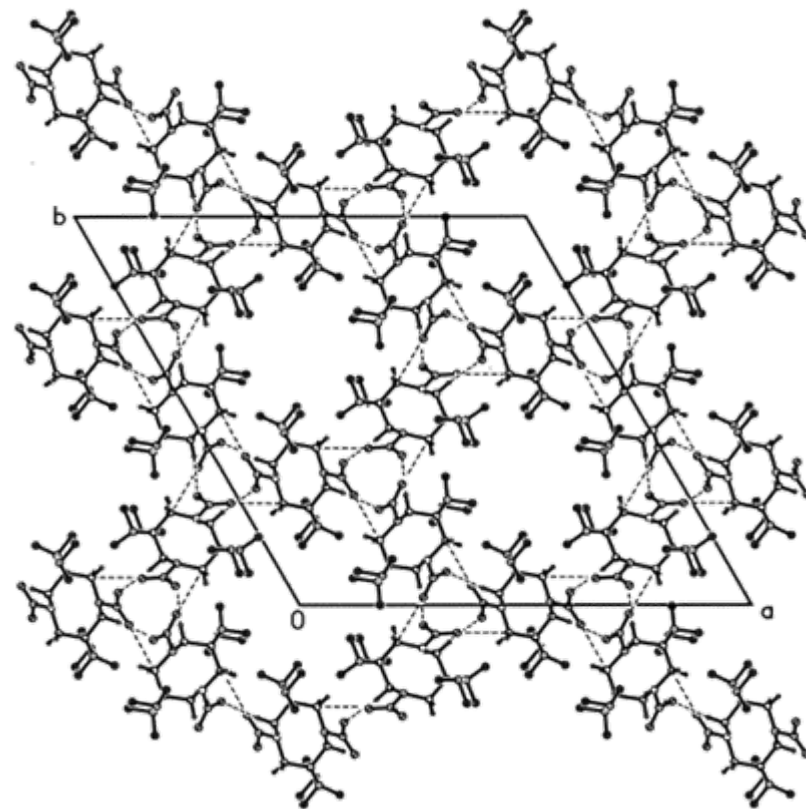- Decompression returns the ambient pressure structure with lower density!

Research and Technology Department

Dynamics and Diagnostics Division, Static High-Pressure Group

High Compressibility of HNFX

Bulk Modulus: 2.0 GPa
Derivative : 44

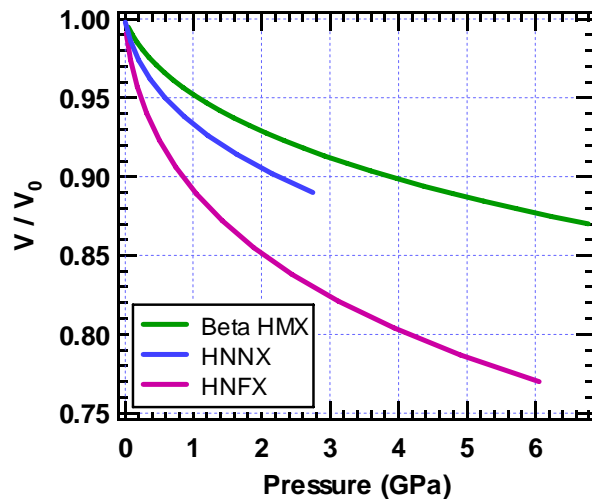Extremely compressible at near-ambient pressure.

Decompresses with a larger volume than pre-compression V_0

A view down the *c* axis showing the packing of HNFX. Empty channels occur along the 3-fold axes at (0,0,z), a corner of the cell, and at (1/3, 2/3, z) and (2/3, 1/3, z) within the cell.
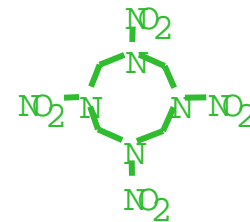From: Chapman, Gillardi et al. *J. Org. Chem.,* **64***,* 963 (1999).

Comparison

β-HMX = Monoclinic structure ρ=1.91 g/cc
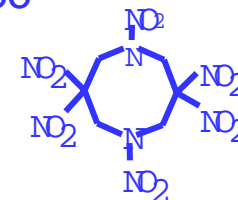Bulk Modulus: 8.9 GPa
Compressibility = 0.11
Derivative: 46.5

HNNX = Orthorhombic structure ρ=1.86 g/cc
Phase transition at 2.2 GPa
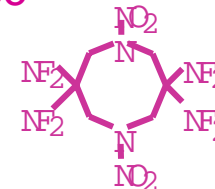Bulk Modulus: 7.46
Compressibility = 0.14
Derivative = 20.0 ± 7.3

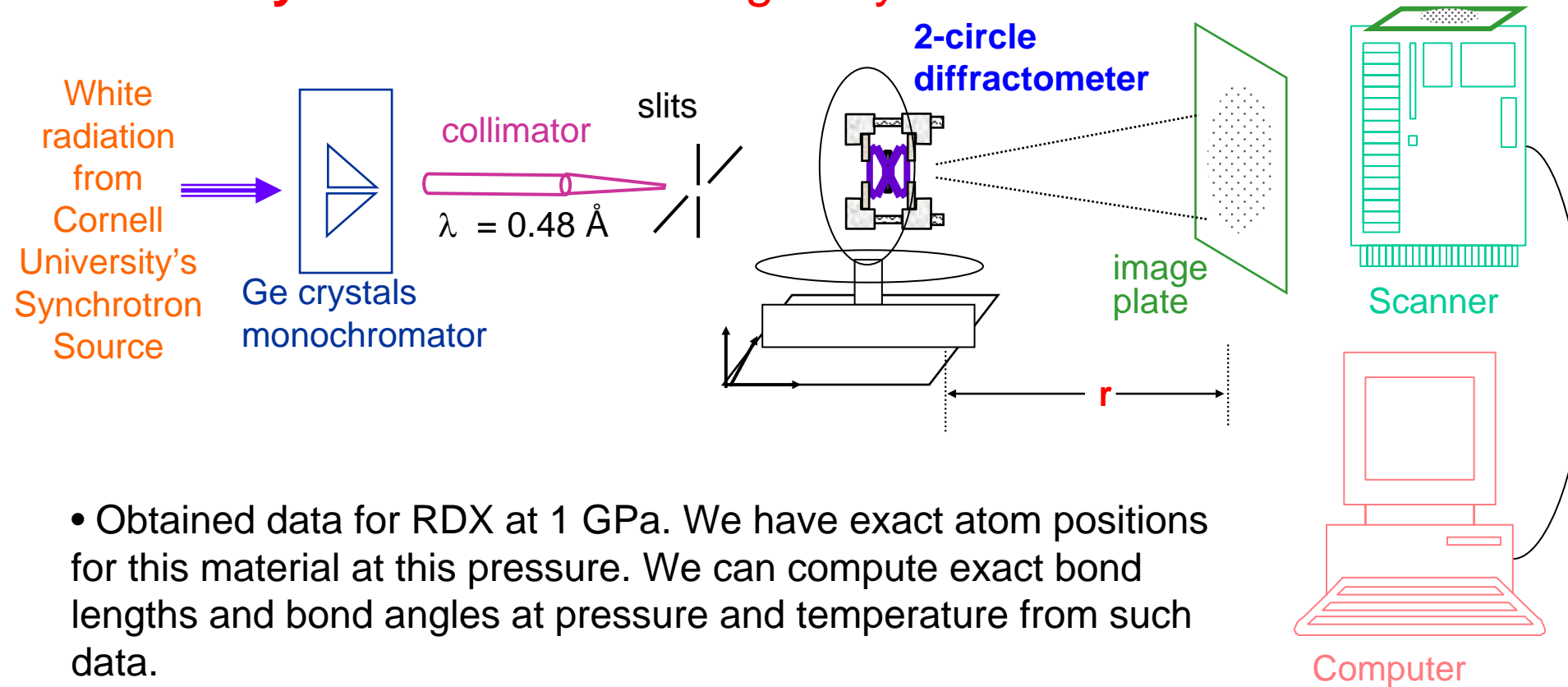HNFX = Rhombohedral structure ρ=1.81 g/cc
Bulk Modulus: 2.0 GPa
Compressibility = 0.50
Derivative : 44.3

Preliminary Results - RDX single crystal diffraction

White radiation from Cornell University's Synchrotron Source

Ge crystals monochromator

collimator

λ = 0.48 Å

slits

2-circle diffractometer

image plate

Scanner

Computer

r

- Obtained data for RDX at 1 GPa. We have exact atom positions for this material at this pressure. We can compute exact bond lengths and bond angles at pressure and temperature from such data.

- Previously published phase transition of RDX at 3.5 GPa to a high-pressure phase.

- We intend to find the lattice symmetry of this high pressure and identify that phase.

NAVSEA
INDIAN HEAD
Surface Warfare Center Division

Research and Technology Department

Dynamics and Diagnostics Division, Static High-Pressure Group
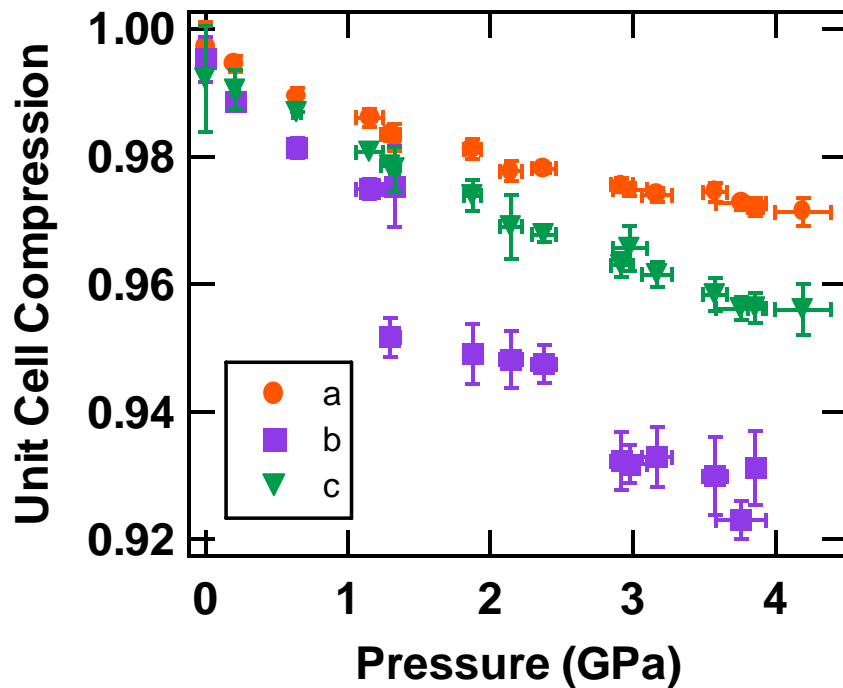
Compression of FOX-7 at ambient temperature: Lattice and molecular symmetry changes

FOX-7 = DiAmino DiNitro Ethylene (DADNE)

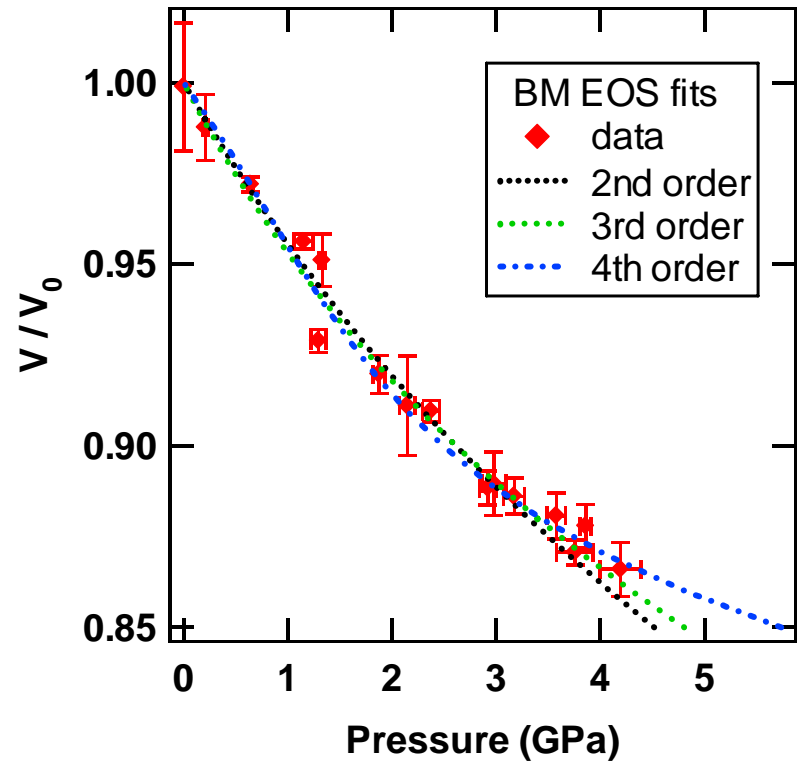$$NH_2 - C = C - NO_2$$
$$NH_2 \quad\quad NO_2$$
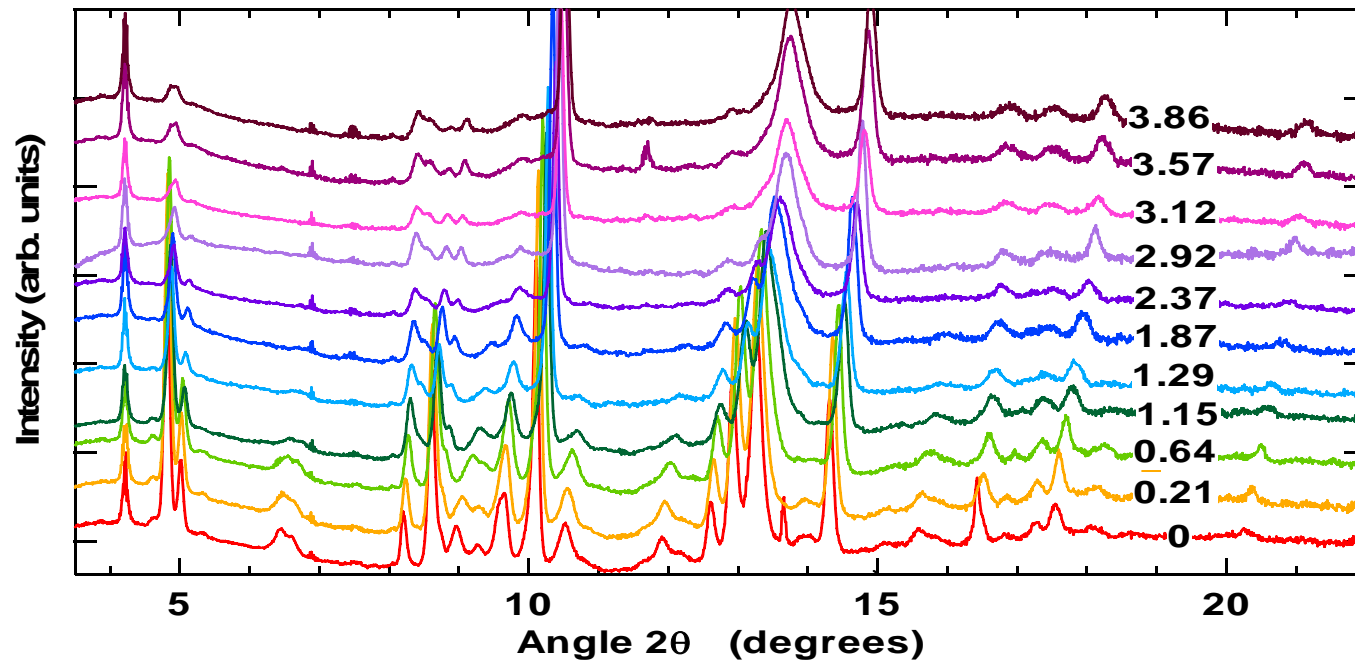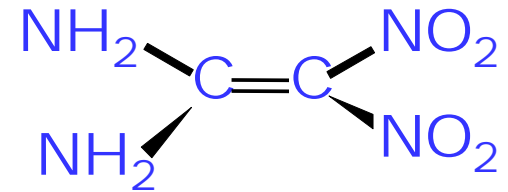
- Monoclinic lattice is stable to 4.2 GPa (possibly a transition above 5 GPa)
- Some peaks indicate faster compression than others = **anisotropic compression**

• Above 1.1 GPa, the "b" axis (inter layer) compresses faster than the "a" or "c".

• Anisotropic compression but no change in lattice symmetry

Birch-Murnaghan : 3rd order
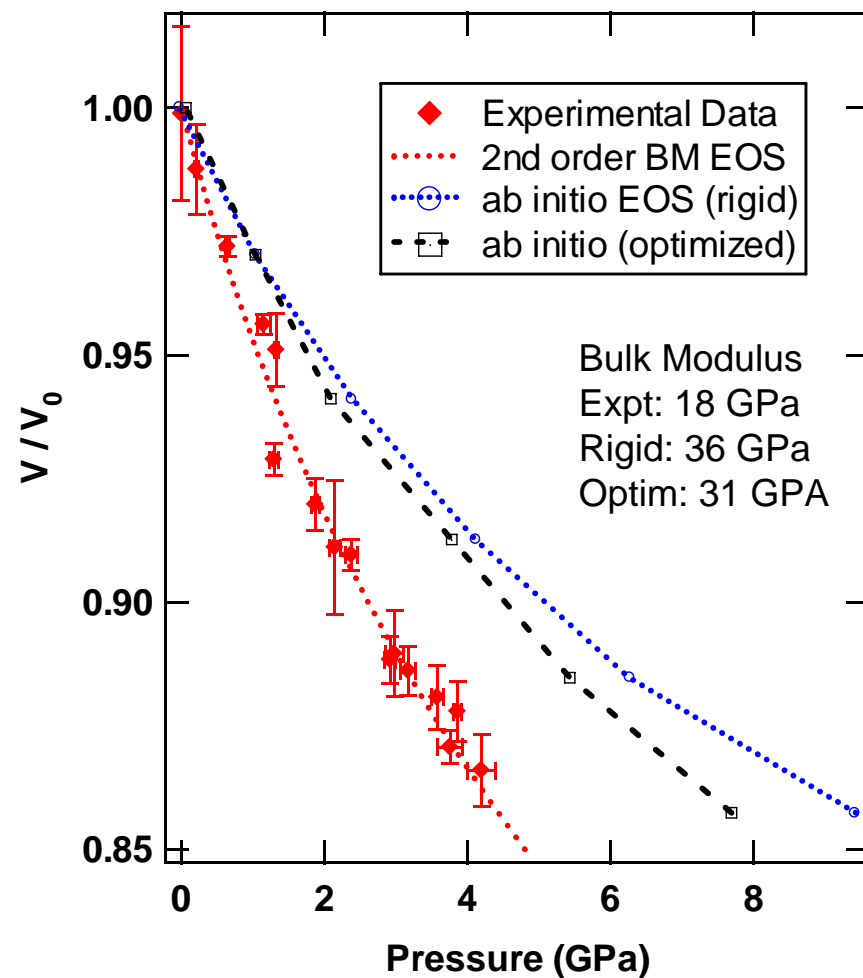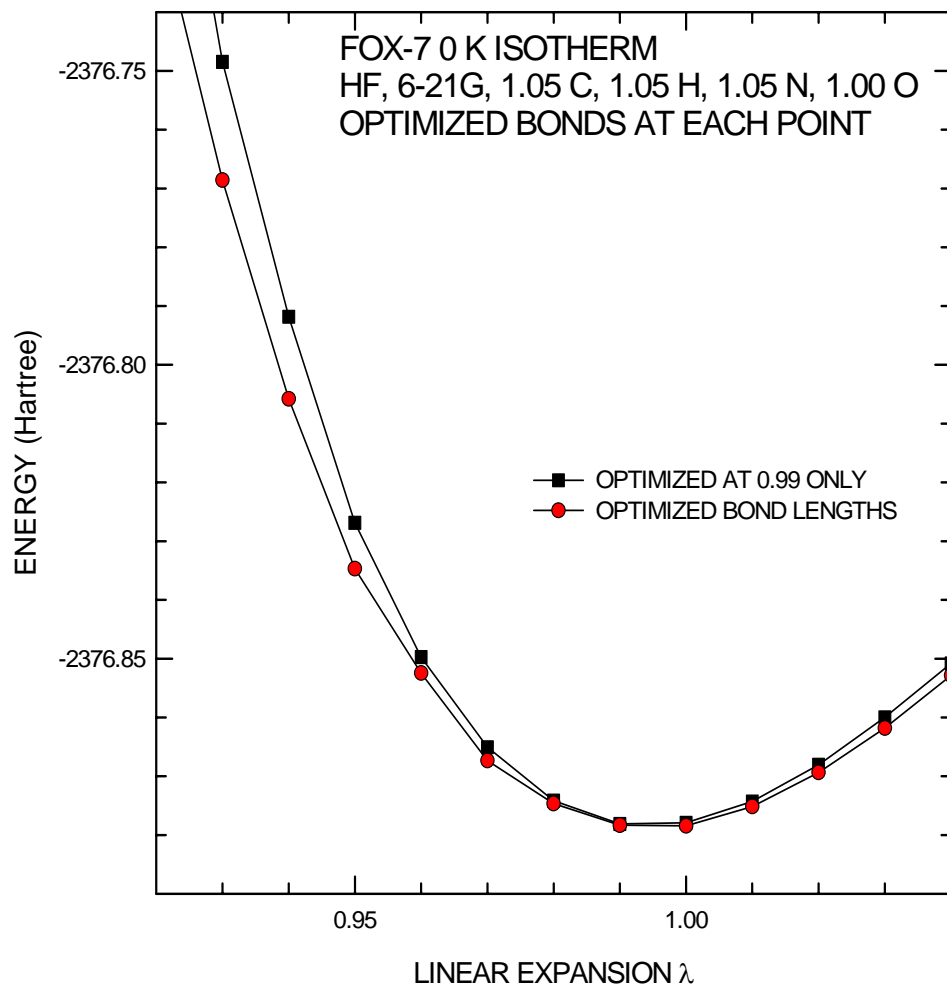
$K_0 = 17.9 \pm 1.4$ GPa

$K_0{'} = 6.6 \pm 4.2$

Latest results indicate a phase transition in FOX-7 at above 5 GPa, at room temperature - the data is not yet analyzed completely.

Ab-initio Hartree-Fock Isothermal (0K) EOS Calculations using Gaussian 98

- simple rigid-molecule approximation
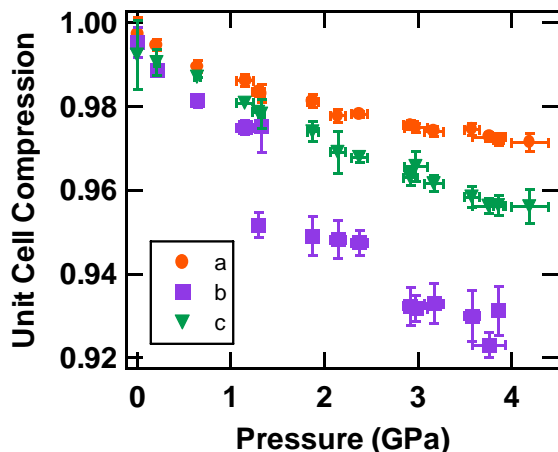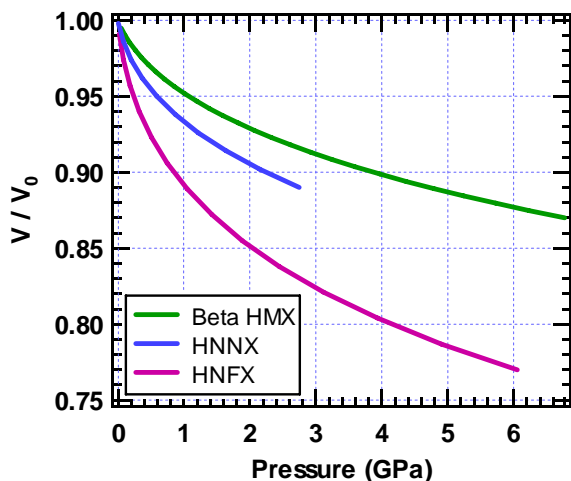- molecule (bonds and angles) optimized using Crystal 98

Calculations by Dr. F. J. Zerilli and M. M. Kukla

FOX-7 0 K ISOTHERM
HF, 6-21G, 1.05 C, 1.05 H, 1.05 N, 1.00 O
OPTIMIZED BONDS AT EACH POINT

ENERGY (Hartree)

OPTIMIZED AT 0.99 ONLY
OPTIMIZED BOND LENGTHS

LINEAR EXPANSION λ

V/V_0

Experimental Data
2nd order BM EOS
ab initio EOS (rigid)
ab initio (optimized)

Bulk Modulus
Expt: 18 GPa
Rigid: 36 GPa
Optim: 31 GPA

Pressure (GPa)

Conclusions

• We are just beginning to understand the effect of high P and T. These effects will be greater as P and T approach that of detonation.

• Experimental and ab-initio EOS and lattice symmetry studies for **HMX**, **HNNX** and **HNFX** show a phase transition in HNNX, with HNFX being extremely compressible.

• Ab-initio calculations show that accuracy for molecules more complex than HMX require less assumptions

• **FOX-7** experiments show anisotropic compression with a discontinuous change at about 1.1 GPa. Other vibrational mode shifts show increased H-bonding. Symmetry changes above 5 GPa are being investigated.

• Ab-initio calculations with optimized bonds do result in better fits to real data